

PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT (PCT Article 36 and Rule 70)

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Applicant's or agent's file reference AN-1010/901/961		FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)	
International application No. PCT/PL 03/00040	International filing date (day/month/year) 17.04.2003	Priority date (day/month/year) 26.06.2002	
International Patent Classification (IPC) or both national classification and IPC C30B9/00			
Applicant AMMONO SP. Z.O.O.			

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
 - ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 5 sheets.

3. This report contains indications relating to the following items:
 - I ☒ Basis of the opinion
 - II ☐ Priority
 - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - IV ☐ Lack of unity of invention
 - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - VI ☐ Certain documents cited
 - VII ☐ Certain defects in the international application
 - VIII ☐ Certain observations on the international application

Date of submission of the demand 15.01.2004	Date of completion of this report 16.11.2004
Name and mailing address of the International preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer Cook, S Telephone No. +31 70 340-3372



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/PL 03/00040**

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1-28 as originally filed

Claims, Numbers

1-30 received on 21.09.2004 with letter of 20.09.2004

Drawings, Sheets

1/8-8/8 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/PL 03/00040

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-20
	No: Claims	21-24
Inventive step (IS)	Yes: Claims	1-20
	No: Claims	21-24,25-30
Industrial applicability (IA)	Yes: Claims	1-30
	No: Claims	

2. Citations and explanations

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/PL 03/00040

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following document:

D1: FR-A-2796657 (THOMSON CSF Société anonyme -FR)

Independent process claims 1 and 2

The subject matter of claims 1-20 appears to meet the criteria of Article 33(1) PCT, because it is new in the sense of Article 33(2) PCT.

Document D1, considered the closest prior art, teaches a process for obtaining bulk gallium containing nitride monocrystals from a supercritical ammonia-containing solution in the presence of the mineralizer. The processes of independent claims 1 and 2 of the present application differ from that of D1 in that the teaching of D1 does not specifically teach the measure of including a Group I element azide when growing the bulk gallium nitride monocrystal. In D1, an initial process for preparing microcrystallites of GaN is described and the use of sodium azide is not recommended. In the crystal growth stage, mention is made of using MN_2 but specifically only Li_3N (tri-lithium nitride) is mentioned. The subject-matter of claims 1 and 2 (and also 3-20) is thus considered novel with respect to the teaching of D1.

The subject matter of claims 1-20 appears to satisfy the criteria set forth in Article 33(3) PCT with regard to inventive step. The applicant has found certain advantages in using alkali metal azides as mineralisers in the ammonothermal process for producing bulk gallium containing nitride monocrystals. These include improved impurity control (particularly oxygen levels). Given the teaching away from using alkali metal azides in D1, it would appear that the process of the present application involves an inventive step.

Independent product claim 21, use claim 22, and product claim 25

In accordance with section 5.26, Chapter 5 and appendix A5.26[1] (as applied by the EPO) of the PCT International Search and preliminary examination guidelines (March 25, 2004), product claim 21 is construed as a claim to the product *per se*. The wording of this claim contains no features which render the subject matter novel with respect to prior art (e.g. D1) teachings of bulk nitride monocrystal products. The wording "*reduced content of impurities, especially oxygen*" is vague and does not clearly define the subject matter as required by Article 6 PCT. The word "*especially*" is non limiting.

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

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Concerning independent claim 22 and its dependent claims 23 and 24, the document D1 implicitly teaches using bulk nitride monocrystals as substrates for epitaxy in the subsequent device manufacture (see page 1 of D1). The subject matter of claims 22-24 cannot be considered as novel or at least inventive.

Concerning the subject matter of independent product claim 25, the observations made for claim 21 apply here also with regard to the PCT guidelines. Simple mixtures of known compounds in arbitrary molar ratios cannot in themselves amount to inventive subject matter.

Industrial applicability

The subject matter of claims 1-30 is considered to meet the requirements of Article 33(4) PCT.

EPO - DG 1

21. 09. 2004

Claims:

(71)

1. Process for obtaining bulk gallium-containing nitride monocrystals from supercritical ammonia-containing solution in the presence of a mineralizer, characterized in that in a pressurized reaction vessel - using ammonia as solvent and Group I element azides and optionally Group II element azides as mineralizer, a supercritical ammonia-containing solution including Group I and optionally Group II element ions is first obtained to dissolve next a gallium-containing feedstock at dissolution temperature and/or dissolution pressure and then the desired gallium-containing nitride is crystallized from the supercritical solution on the surface of at least one seed at the crystallization temperature and/or crystallization pressure, wherein the crystallization temperature and/or crystallization pressure is selected according to the temperature coefficient of solubility and pressure coefficient of solubility of the desired gallium-containing nitride to be crystallized.
2. Process for obtaining bulk gallium-containing nitride monocrystals from supercritical ammonia-containing solution in the presence of Group I and optionally Group II element-containing mineralizer, characterized in that when gallium-containing nitride has a negative temperature coefficient of solubility and a positive pressure coefficient of solubility in supercritical ammonia-containing solution, in the presence of Group I and optionally Group II element-containing mineralizer, in a pressurized reaction vessel - using Group I element azides and optionally Group II element azides as mineralizers - supercritical ammonia-containing solution including Group I and optionally Group II element ions is first obtained to dissolve next a gallium-containing feedstock at dissolution temperature and/or dissolution pressure and then gallium-containing nitride is crystallized from the supercritical solution on the surface of at least one seed by means of bringing the temperature to crystallization temperature and/or the pressure to crystallization pressure, the crystallization temperature being higher than the dissolution temperature and/or the crystallization pressure being lower than the dissolution pressure at least at the crystallization zone of the pressurized reaction vessel, where

the seed is placed – so that super-saturation of the supercritical solution with respect to the seed is achieved - and then the super-saturation of the supercritical solution is maintained at the level at which spontaneous crystallization of the nitride may be neglected, while crystallization of the desired gallium-containing nitride is carried out on the seed.

3. Process according to claim 1 or 2, characterized in that the gaseous nitrogen, produced during the decomposition of the azide, is at least partially evacuated from the system before the re-crystallization step is started.
4. Process according to any one of the preceding claims 1 to 3, characterized in that as a gallium-containing nitride - the nitride having a general formula $Al_xGa_{1-x}N$, where $0 \leq x < 1$ is crystallized.
5. Process according to any one of the preceding claims 1 to 4, characterized in that the azide mineralizers are selected from the group consisting of LiN_3 , NaN_3 , KN_3 , CsN_3 and mixtures thereof.
6. Process according to any one of the preceding claims 5, characterized in that the mineralizer used contains at least one compound selected from the group consisting of LiN_3 , NaN_3 , KN_3 and CsN_3 .
7. Process according to the claim 6, characterized in that the mineralizer contains NaN_3 and KN_3 mixed in arbitrary molar ratio.
8. Process according to the claim 6, characterized in that the mineralizer contains NaN_3 and LiN_3 mixed in arbitrary molar ratio.
9. Process according to the claim 6, characterized in that the mineralizer contains KN_3 and LiN_3 mixed in arbitrary molar ratio.
10. Process according to the claim 6, characterized in that the mineralizer contains also Group I and optionally Group II element-containing compound(s) other than azides.

11. Process according to any one of the preceding claims 1 to 10, characterized in that Group I element azides are introduced into the system in a molar ratio of azides to ammonia ranging from 1:200 to 1:2.
12. Process according to any one of the preceding claims 1 to 11, characterized in that a seed crystal with at least a crystalline layer of Group XIII element nitride, preferably gallium-containing nitride, having a dislocation density less than $10^7 / \text{cm}^2$ is used.
13. Process according to any one of the preceding claims 1 to 12, characterized in that a structure having a number of surfaces spaced adequately far from each other, arranged on a primary substrate and susceptible to the lateral overgrowth of crystalline nitrides is used as a seed.
14. Process according to any one of the preceding claims 1 to 13, characterized in that a monocrystalline nitride layer is obtained having the same or better quality as it gets thicker.
15. Process according to claims 13 or 14, characterized in that the seed contains the primary substrate made of a crystalline nitride of Group XIII elements.
16. Process according to claim 15, characterized in that the seed contains the primary substrate made of gallium nitride – GaN.
17. Process according to claim 15, characterized in that the seed contains the primary substrate made of a crystalline material such as sapphire, spinel, ZnO, SiC or Si, wherein the primary substrate made of the material reacting with a supercritical ammonia-containing solution is covered with a protective layer, preferably made of a nitride containing Group XIII elements or metallic Ag, prior to formation of a monocrystalline nitride layer.
18. Process according to any one of the preceding claims 1 to 3, characterized in that the bulk nitride monocrystals obtained consist essentially of gallium nitride – GaN.

19. Process according to any one of the preceding claims 1 to 3, characterized in that the bulk nitride monocrystals obtained contain any of the following elements: Ni, Cr, Co, Ti, Fe, Al, Ag, Mo, W, Si and Mn.
20. Process according to any one of the preceding claims 1 to 3, characterized in that some surfaces of the seed are covered with a mask layer prior to formation of a monocrystalline nitride layer.
21. A bulk nitride monocrystal obtained by a process according to any one of the preceding claims 1 to 20, having reduced content of impurities, especially oxygen.
22. Use of the bulk nitride monocrystal according to claim 21 as substrate for epitaxy.
23. Use according to claim 22, characterized in that the bulk nitride monocrystal has at least one epitaxial layer of the same or different Group XIII element nitride, deposited by MOCVD or HVPE or else MBE method - as a template for opto-electronic devices.
24. Use according to claim 23, characterized in that MOCVD or HVPE or else MBE nitride layers are doped with various dopants.
25. Mineralizer for use in a process according to anyone of the preceding claims 1-20 which comprises at least two compounds selected from the group consisting of LiN_3 , NaN_3 , KN_3 , and CsN_3 .
26. Mineralizer according to the claim 25, which contains NaN_3 and KN_3 in arbitrary molar ratio of NaN_3 to KN_3 .
27. Mineralizer according to the claim 25, which contains NaN_3 and LiN_3 in arbitrary molar ratio of NaN_3 to LiN_3 .
28. Mineralizer according to the claim 25, which contains KN_3 and LiN_3 in arbitrary molar ratio of KN_3 to LiN_3 .
29. Mineralizer according to the claim 25, which contains NaN_3 , KN_3 and LiN_3 in arbitrary molar ratio of NaN_3 to KN_3 and LiN_3 .

30. Mineralizer according to the claim 25, which further contains Group I and optionally Group II element-containing compound(s) other than azides and/or Group I element, and/or Group II element.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/PL 03/00040

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C30B9/00 C30B29/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C30B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 796 657 A (THOMSON CSF) 26 January 2001 (2001-01-26) cited in the application page 6, line 10 -page 8, line 18	1,2,4-6, 21-25
A	WO 98 55671 A (GRZEGORY IZABELLA ;KRUKOWSKI STANISDAW (PL); WROBLEWSKI MIROSDAW () 10 December 1998 (1998-12-10) the whole document	
A	US 6 177 057 B1 (PURDY ANDREW P) 23 January 2001 (2001-01-23) -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the International filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the International filing date but later than the priority date claimed

- *T* later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *Z* document member of the same patent family

Date of the actual completion of the International search

25 September 2003

Date of mailing of the International search report

06/10/2003

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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KETCHUM D R ET AL: "Crystal growth of gallium nitride in supercritical ammonia" JOURNAL OF CRYSTAL GROWTH, NORTH-HOLLAND PUBLISHING, AMSTERDAM, NL, vol. 222, no. 3, January 2001 (2001-01), pages 431-434, XP004314417 ISSN: 0022-0248 cited in the application	
A	DWILISKI ET AL: "AMMONO method of BN, AlN and GaN synthesis and crystal growth" MRS INTERNET JOURNAL NITRIDE SEMICONDUCTOR RESEARCH, 'Online!' vol. 3, no. 25, 1998, XP002235467 Retrieved from the Internet: <URL:http://nsr.mij.mrs.org/3/25> 'retrieved on 2003-03-20! cited in the application the whole document	
A	YANO M ET AL: "CONTROL OF NUCLEATION SITE AND GROWTH ORIENTATION OF BULK GAN CRYSTALS" JAPANESE JOURNAL OF APPLIED PHYSICS, PUBLICATION OFFICE JAPANESE JOURNAL OF APPLIED PHYSICS. TOKYO, JP, vol. 38, no. 10A, PART 2, 1 October 1999 (1999-10-01), pages L1121-L1123, XP000891127 ISSN: 0021-4922	
A	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 05, 30 April 1998 (1998-04-30) & JP 10 007496 A (HITACHI CABLE LTD), 13 January 1998 (1998-01-13) abstract	
A	GB 2 326 160 A (HITACHI CABLE) 16 December 1998 (1998-12-16)	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/PL 03/00040

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FR 2796657	A	26-01-2001	FR 2796657 A1	26-01-2001
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